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RESEARCH PROGRESS ON GROWTH OF UV  
NONLINEAR OPTICAL BORATE CRYSTALS

by

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RESEARCH PROGRESS ON GROWTH OF UV  
NONLINEAR OPTICAL BORATE CRYSTALS

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ABSTRACT:

In this paper, a description of research advance on the growth of some important uv nonlinear optical crystals, such as BBO, LBO and KBBF etc. , which were first invented and developed by our institute during the past decade is given. The review consists of the following contents: the choice of method for the crystal growth; the technique of the crystal growth and the development; the choice of the flux; the effects of the solution structure and other growth conditions on the crystal growth; the metastable growth of BBO crystals and BBO crystal growth from the pure melt by a direct CZ method; the habit and defect of the crystal and other important problems in the crystal growth.

For a long time, searching for ultraviolet nonlinear optical materials with excellent properties has always been an area of highest interest for scientists in China and abroad. Therefore, after the publication of the first ultraviolet nonlinear optical crystal low-temperature phase barium metaborate  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (briefly

called BBO) with important applications [1], great interest was evoked in the international sphere of science and technology. Many scientists in developed countries competed in advancing research tasks on BBO crystal structure, performance, and growth [2-11]. The paramount feature of the BBO crystal is its application in ultraviolet irradiation with wavelengths as short as 200nm [4]. BBO is the only crystal with quadruple frequency to deep ultraviolet 0.265 $\mu$ m capable of being used in a 1.06 $\mu$ m Nd:YAG laser. After BBO, the Institute of Research on the Structure of Matter made available in 1989 the second China-brand ultraviolet nonlinear optical crystal lithium triborate  $\text{LiB}_3\text{O}_5$  (briefly, LBO) [12]. The greatest advantage of the LBO crystal is its very high optical damage threshold value, capable of carrying out 90° noncritical-phase matching. At present, LBO crystals have been extensively applied in frequency doubling and tripling in high-power Nd:YAG laser devices, as well as optical parametric amplifiers (OPO) [3]. Potassium beryllium borate fluoride ( $\text{KBe}_2(\text{BO}_3)\text{F}_2$  [briefly, KBBF]) is another kind of ultraviolet nonlinear ultraviolet crystal recently developed at the institute. This crystal is at present the only crystal capable of doubling frequencies lower than 200nm, and this crystal can be used in phase-matching up to 177.3nm. At present, the doubled-frequency light of 184.7nm has been obtained with the crystal [14]. The article mainly discusses progress in research on growing these crystals.

## I. Selecting and Developing the BBO Crystal-Growing Method

### 1.1. Two-phase conversion of BBO crystal and growing it with the flux method

There are two  $\text{BaB}_2\text{O}_4$  crystallization phases: high-temperature  $\alpha$  phase and low-temperature  $\beta$ -phase. The single-level phase variation temperature is approximately  $925^\circ\text{C}$  [15,16]. The  $\alpha$  phase is centrosymmetrical; the space group is  $D_{3d}^6-R\bar{3}c$ . However, the  $\beta$ -phase is noncentrosymmetric; its space group is  $C_{3v}^2-R3C$  [17]. In the latter case, there is a strong nonlinear optical effect. The melting point of the same constituents of  $\text{BaB}_2\text{O}_4$  is  $1095^\circ\text{C}$ . To avoid problems in the growth high-temperature phase and from the  $\alpha$ - $\beta$  phase transition, generally  $\beta$ -phase crystals are grown by the flux method, in other words, an appropriate amount of flux is required to reduce the growth temperature below the phase-transition temperature. There have been many reports on the flux selection for BBO, in addition, to  $\text{Na}_2\text{O}$  [8,9,18-21], there are  $\text{NaCl}$  [22,23],  $\text{NaCl-Na}_2\text{O}$  [22], and  $\text{Na}_2\text{O-NaF}$  [24] fluxes. As indicated in our research,  $\text{Na}_2\text{O}$  and  $\text{NaF}$  are two appropriate fluxes, with appropriate constituent composition as  $(0.75-0.80)$  mol  $\text{BaB}_2\text{O}_4$  :  $(0.25-0.20)$  mol  $\text{Na}_2\text{O}$   $(0.65-0.70)$  mol  $\text{BaB}_2\text{O}_4$  :  $(0.35-0.30)$  mol  $\text{NaF}$ . Crystals can be grown by the molten salt seed crystal method and the molten salt pulling method. By using these two methods, we have grown large and high-quality BBO single crystals.

### 1.2. Metastable phase growth of $\beta$ - $\text{BaB}_2\text{O}_4$ crystals

Based on the phase diagram of  $\text{BaB}_2\text{O}_4$ - $\text{Na}_2\text{O}$  crystals, the appropriate range for the constituent composition of BBO growth

should be 20 to 30 mol%  $\text{Na}_2\text{O}$  [25]. However, this is not so in actual cases of crystal growth. In research by Tang Dingyuan et al. on the growth of BBO single-crystal whiskers by the laser-heated seed method, it was discovered that by adding a very small amount (approximately 3mol%) of  $\text{Na}_2\text{O}$ ,  $\beta\text{-Ba}_2\text{O}_4$  single-crystal whiskers can still be grown. It was also discovered that these single-crystal whiskers were in the  $\alpha$  phase when the  $\alpha$ -phase crystal was used as the seed crystals. By using  $\beta$ -phase crystals as the seed crystals,  $\beta$ -phase single-crystal whiskers can be grown [26]. Later, the Japanese scientist Onishi reported for the first time the use of the  $\mu\text{-CZ}$  method in growing  $\beta$ -phase BBO single-crystal whiskers [27] from a pure melt without adding any flux. Successively, Ito et al. reported on the use of the pulling method to directly grow 7mm-diameter, 80mm-long  $\beta\text{-Ba}_2\text{O}_4$  single crystals [18] from a  $\text{BaB}_2\text{O}_4$  melt. This method was also applied by Kouta et al. to grow large (15mm in diameter and 40mm in length)  $\beta\text{-BaB}_2\text{O}_4$  single crystals [29]. As indicated by numerous studies,  $\beta\text{-BaB}_2\text{O}_4$  crystals can be grown at temperatures higher than the phase-transition temperature  $T_{\alpha-\beta}$  and can even be grown from a pure melt. The growth rate is scores or hundreds of times faster than when flux is used. The typical growth rate in the pulling method is 2 to 4mm/h [29]; with the molten salt method, the growth rate is 0.5-1mm/day [19]. In addition, a major advantage of pure-melt growth is the avoidance of contamination from flux impurities, thus obtaining higher-quality single crystals, with a threshold value to optical damage as high as  $26\text{GW}/\text{cm}^2$  [31]. This is a great

breakthrough in growth techniques. Undoubtedly, the growth of  $\beta$ - $\text{BaB}_2\text{O}_4$  above the phase-transition temperature is growth of the metastable phase. The crystal growth in the metastable phase can be illustrated by using Ostwald's Step rule [32]. At temperatures lower than the supercooling temperature, growth of metastable phase is possible for solutions that are readily supercooled. Fig. 1 shows the  $\text{BaB}_2\text{O}_4$  melt, the relation between Gibbs' free energy and

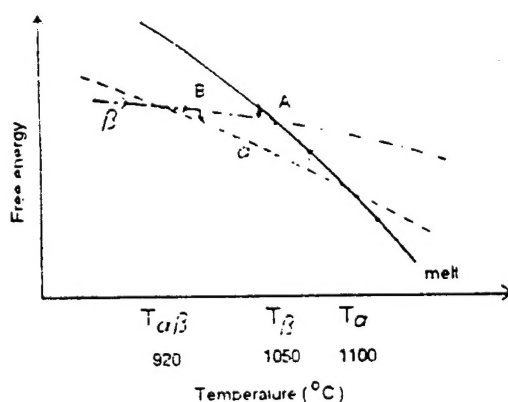


Fig. 1. Curve of free energy versus temperature in the  $\alpha$ -,  $\beta$ -, and melt phases of BBO

temperature of the  $\alpha$  and  $\beta$  phase [33]. From the figure, we can see that  $Z_{\beta} < Z_{\alpha}$  at a temperature under the phase transition temperature. Therefore, the  $\beta$ -phase is the stable crystallized phase. When the temperature is between  $T_{\alpha-\beta}$  and  $1050^\circ\text{C}$ , although  $Z_{\beta} > Z_{\alpha}$ , yet the temperature is still lower than that of the  $Z_{\text{melt}}$ . Therefore, the  $\beta$ -phase can still crystallize into the metastable phase. However, when the temperature exceeds  $1050^\circ\text{C}$ , since  $Z_{\beta} > Z_{\text{melt}}$ ,  $\beta$ -phase crystallization cannot be carried out. The reason for supercooling is closely related to the structure and properties of the solution.



With respect to the BBO melt, besides the higher viscosity, the elementary structure of the melt is also an important factor affecting growth. Recently, a Russian scientist, Voronko, and an American scientist, Feigelson [34], cooperated for the first time to apply high-temperature Raman spectral (HTRS) method to study the relationship between the structure of the boron oxygen radical in the borate-system solution and the crystallization of borate. They discovered that  $(B_2O_6)$  and the longer chain  $(BO_2)_n$  mainly exist in the  $BaB_2O_4$  melt. The value of  $n$  increases with a rise in temperature. They also applied this method to conduct an in-situ study on the spontaneous nucleation in the BBO melt. It was discovered that the spontaneous crystallization of BBO can occur only when there are certain quantities of  $(B_3O_6)$  ring radical present in the melt. Because at the melting point  $BaB_2O_4$  contains  $(BO_2)_n$ , therefore, spontaneous crystallization does not occur until there is supercooling at 150 to 200°C. At this point, sufficient amounts of  $(B_3O_6)$  are present. In the studies by the Japanese scientists, the key to growing  $\beta$ -phase BBO crystals in a melt is preparation of the starting materials. Only by using starting materials prepared by some method, can  $\beta$ -phase BBO be grown. In their view, these starting materials maintain the  $\beta$ -phase structure. Table 1 shows the effects on the crystallization-phase of the starting-material preparatory process.

How is it that  $\beta$ -phase BBO crystals can be grown from a pure? One explanation is that the  $\beta$ -phase structure is maintained in the growth solution under certain conditions. By using the molecular

dynamic simulation method (MD), Ogawa [39] studied the structure of the BBO solution immediately after melting. He discovered that the

TABLE 1. Effect on Crystallization Phase due to Starting Materials

BaB <sub>2</sub> O <sub>4</sub> 原料的制备方法	1	2 结晶相	参考文献 3
(1) BaCO <sub>3</sub> + 2H <sub>3</sub> BO <sub>3</sub> → BaB <sub>2</sub> O <sub>4</sub> + CO <sub>2</sub> + 3H <sub>2</sub> O		$\alpha$	[27, 29]
(2) BaCl <sub>2</sub> + 2NaBO <sub>2</sub> → BaB <sub>2</sub> O <sub>4</sub> + 2NaCl		$\beta$	[28]
(3) BaCl <sub>2</sub> · 2H <sub>2</sub> O + 2H <sub>3</sub> BO <sub>3</sub> → BaB <sub>2</sub> O <sub>4</sub> · 4H <sub>2</sub> O + 2HCl		$\beta$	[29]
BaB <sub>2</sub> O <sub>4</sub> · 4H <sub>2</sub> O → BaB <sub>2</sub> O <sub>4</sub> + 4H <sub>2</sub> O			
(4) $\alpha$ 相单晶	4	$\alpha$	[30]
(5) $\beta$ 相单晶	5	$\beta$	[30]

KEY: 1 - method of preparing BaB<sub>2</sub>O<sub>4</sub> starting material  
 2 - crystallization phase 3 - reference 4 -  $\alpha$ -phase  
 single crystals 5 -  $\beta$ -phase single crystals

properties of the (30 $\bar{3}$ 0) periodic fundamental structures observed in the  $\beta$ -phase crystal was maintained in the liquid crystal immediately after melting for the  $\beta$ -phase crystal. However, there was no discovery of such periodic properties in the liquid after the melting of the  $\alpha$ -phase crystal. The difference in liquid structure between the  $\alpha$  and  $\beta$ -phases may affect the atomic dynamics in the crystal growth process. From the theoretical approach of phase transition, the potential energy is lower during phase transition for the similar radical structure, therefore the phase transition is more easily carried out.

## II. Important Problems in Growth of BBO Crystals

### 2.1. Effect on Crystal Cleavage with Seed Crystal Orientation [36]

As indicated in experiments, the direction of crystal growth has obvious effects on cleavage of BBO crystals. If seed crystals with a or b axis along the direction deviate greatly from the c-axis, serious cleavage will occur in the crystals. The cleavage is along the (0001) cleavage surface perpendicular to the c-axis direction with cleavage into many parallel chips. However, the crystals are not easily cleaved if grown along the c-axis, then high-quality single crystals free of any cleavage can be obtained. An important reason for causing cleavage in BBO crystals is that its coefficient of thermal expansion appears in the anisotropic difference. Fig. 2 shows the results of determining the

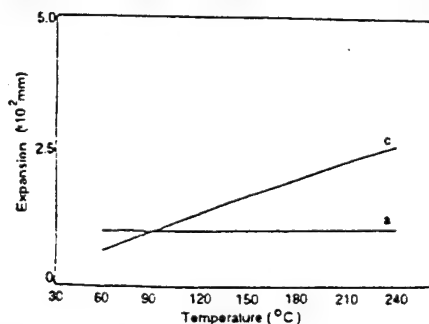


Fig. 2. Thermal expansion curve of BBO crystals coefficients of thermal expansion along the a- and c-axes of BBO crystals by using thermal expansion instruments. When grown along the direction of the a- or b-axes, anisotropic shrinkage of the crystal in the annealing and cooling process will occur in the diametral direction; this surface is the b- (or a-) c-type. Here, since shrinkage along the c-direction is much greater than along the b-direction, cleavage perpendicular to the c-direction occurs.

If the growth along the c-direction is applied, the shrinkage surface ab is isotropic, therefore cleavage does not easily occur. Therefore, use of the c-axis as the direction of growth of BBO crystals is the most advantageous direction [20, 37].

## 2.2. Effect on growth conditions, on the one hand, and on solid-liquid interface shape, and stability, on the other

During the crystal growth process, the solid-liquid interface shape and stability have decisive effects on the crystal growth rate, especially on crystal quality. To obtain high-quality single crystals, generally a flat or slightly convex growth interface should be adopted. There have numerous research reports on the solid-liquid interface problem for crystal growth in melts. However, there are fewer research reports on the liquid-solid interface for liquid growth in high-temperature solutions. In [37], this was the first report on the effect of interface shape in the BBO crystal growth process due to growth conditions in growing BBO crystals by the pulling method in molten salts. Table 2 gives

TABLE 2. Effect due to Growth Conditions on Solid-Liquid Interface Shape on BBO Crystal Growth

Crystal diameter (mm)	Rotation rate (rpm)	Pulling rate (mm/day)	Cooling rate (°C/day)	Interface shape
20	10	0.6	1.0	Convex
26	5	0.9	0.8	Flat
40	5	0.5	0.8	Convex
40	6	0.8	0.5	Flat
45	12	0.5	0.8	Concave
48	5	0.8	1.0	Flat
48	7	1.3	0.9	Concave
51	5	0.6	1.0	Flat
55	6	1.0	1.0	Concave
68	2.5	0.0	1.0	Convex
75	4.5	0.0	0.3	Convex
75	25	0.0	1.0	Concave

some typical results. From the table, we see that the interface shape varies with the crystal rotation rate and pulling rate. Similar to crystal growth in melts, increasing the rotation rate can cause a transition of the interface to convex to concave. With an increase in crystal diameter, this transition will be more pronounced. In the difference from crystal growth in melts, the crystal pulling rate can also obviously affect interface shape. An excessive pulling rate will cause the transition of the growth interface from convex to concave. We know that when growing crystals in a melt, the main factor deciding the interface shape is the temperature difference at the interface. There are two kinds of convections at the solid-liquid interface for crystal growth: one is natural convection due to the temperature gradient and the floating force, and the other is forced convection due to crystal rotation. When the crystals are fixed, there is only natural convection. Now the flowing direction of the melt is from the edge to the center of the crucible. Thus, the temperature at the edge of the crystal is higher than that of its center. Therefore, a convex interface is caused. When the crystal rotates, there is forced convection with its direction the opposite that of natural convection. As the rotation rate is increased, the weighting of this forced convection is greater and greater, finally causing the appearance of a concave interface. With respect to crystals grown in a high-temperature solution, the main factor deciding the interface shape is the density distribution near the interface. To

phrase it more exactly, this is supersaturation. Supersaturation as such can also be expressed in temperature:  $\Delta T = (t' - t)$ . Here  $t'$  indicates the melt saturation temperature;  $t$  is the actual melt temperature. We can easily see here that as the melt temperature is increased, supersaturation becomes less. Therefore, when the crystal rotation rate is increased, supersaturation at the interface center is reduced, thus causing the transition of the interface from convex to concave. Moreover, another reason for causing variation in interface shape by the crystal rotation rate is that the BBO crystal growth system is a highly viscous melt system. When the crystal rotates, the melt in the lower central portion of the interface more easily forms a vortex liquid cylinder, which spins around its center, thus, the lower central portion of the crystal interface becomes a stagnant region, obviously hindering exchange of melt in this region so that a timely supply of nutrient required for interface growth in the central region is blocked. As indicated in the experiments, the pulling rate not adaptable to the rate of temperature decrease will pull the crystal out of the liquid surface. Therefore, to grow high-quality BBO crystals with the pulling method, we must apply an appropriate rotation rate and a corresponding pulling rate matching the rate of temperature decrease. Generally, when the rotation rate is between 4 and 8rpm, the rate of temperature reduction is between 0.5 to 2.5°C per day, and the pulling rate is between 0.5 and 1.0mm per day. An overrapid rotation rate, and a pulling rate not corresponding to the rate of temperature decrease will cause a

transition of the interface from convex to concave, with unstable interface, and even the destruction of stability in causing defects such as inclusions.

### III. Growth and Defects of LBO Crystals

Compared to BBO crystals, there are fewer reports on the growth of LBO crystals.

#### 3.1. Selection of crystal growth methods

As early as 1958, Sastry and Hummel published a phase diagram of the  $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  binary system [38]. From the phase diagram we can see that the compound  $\text{Li}_2\text{O}:3\text{B}_2\text{O}_3$  will decompose into  $2\text{Li}_2\text{O}\cdot5\text{B}_2\text{O}_3$  ( $\text{Li}_4\text{B}_5\text{O}_{17}$ ) or  $\text{Li}_2\text{O}\cdot2\text{B}_2\text{O}_3$  ( $\text{Li}_2\text{B}_4\text{O}_{17}$ ) at temperatures higher than  $834^\circ\text{C}$ . Therefore, LBO is a compound without consistent melting; the flux method should be applied to grow these crystals. As indicated in many research reports

[39-44], an excessive amount of  $\text{B}_2\text{O}_3$  used as a flux is the most appropriate flux for the growth of LBO crystals. The constituent composition of the growth melt is generally 1mol  $\text{Li}_2\text{O}$ :4mol  $\text{B}_2\text{O}_3$ . High-optical-quality LBO crystals have been grown by using the TSSG method with the above-mentioned constituent composition; the maximum dimensions of crystals that have been grown are  $75\times75\times18\text{mm}$ .

#### 3.2. Effect of seeding temperature on crystal growth

An important problem in growing LBO crystals is to master the seeding temperature. Since the crystal melting point of the LBO

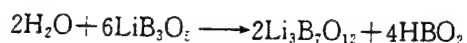
crystal does not differ widely from that of the saturation temperature of the growth melt as that of the BBO, therefore, in LBO crystal growing, higher temperatures will melt the seed crystal before contact with the growth melt. If the temperatures are on the low side, after contact between the seed crystal and the liquid surface, the seed crystal will grow rapidly, resulting in the growth of multiple crystals, thus frequently causing the stability breakdown of the melt, producing large amounts of hetero-crystals floating on the liquid surface. Therefore, while growing LBO crystals, it is required generally to use the seed crystal test method before adding the seed crystals to correctly measure the melt saturation temperature. Then, at a temperature 3 to 5°C higher than the saturation temperature, the seed crystal is added; the initial growth period should be carefully observed and controlled.

### 3.3. Stabilization problem at the surface during LBO crystal growing

In the LBO crystal growth process, sometimes we will discover a layer of white patina on the crystal surface. Generally, this patina begins at the seed crystal, then gradually extends to the edge of the growing crystal. This white patina affects the monitoring of the crystal during its growth, on the one hand, and causes the dropping of the growing crystal due to weakening strength of the seed crystal, on the other. The thicker patina is frequently accompanied with serious cleavage of the crystal. As indicated in the X-ray analysis, this white patina is  $3\text{Li}_2\text{O} \cdot 7\text{B}_2\text{O}_3$



(Li<sub>3</sub>B<sub>7</sub>O<sub>12</sub>) [42]. Brick et al. [45] thought that the formation of this patina is due to the function of water vapor. They applied the DTM method to study the effect on surface stabilization of LBO growth due to water vapor under conditions of dry and wet N<sub>2</sub>. They discovered that the white patina appeared on the growth surface of LBO in wet N<sub>2</sub>, and the crystal weight decreases. However, in dry N<sub>2</sub> this phenomenon does not appear. They concluded that the following reactions occurred due to the presence of water vapor:



This problem also troubled us for quite some time. Later, we discovered that this was due to water leakage from the oven casing since cooling water was required for some ovens. After we cut off the cooling water to the oven jacket, the foregoing problems did not occur.

#### 3.4. Effect on crystal growth due to melt structure [46,47]

As indicated in a study of infrared spectra on the structure of Li<sub>2</sub>O.xBO<sub>3</sub> (2<x<5) melt, different constituent compositions will cause variations in the characteristic absorption peaks 1200 to 1400cm<sup>-1</sup> of elongation and shrinkage oscillations of the BO<sub>4</sub> bonds in the labeled BO<sub>3</sub> radical, and the variation of the characteristic absorption peaks 850 to 1100cm<sup>-1</sup> intensity of elongation and shrinkage oscillations in the B-O bond in the labelled BO<sub>4</sub> radical. With increase in the LiO<sub>2</sub> content and an increase in the peak value in the range between 850 and 1000cm<sup>-1</sup>, the constituents of the labelled BO<sub>4</sub> radical increased. We can see that different compounds will be formed with variation in the constituent

composition ratios. This point was verified in practical crystal-growing. Table 3 lists the effect on the growing crystallization phase and the molecular structure type owing to the constituent composition ratios of the starting material. Fig. 3 indicates the infrared spectrum of the glassy state obtained by quenching the

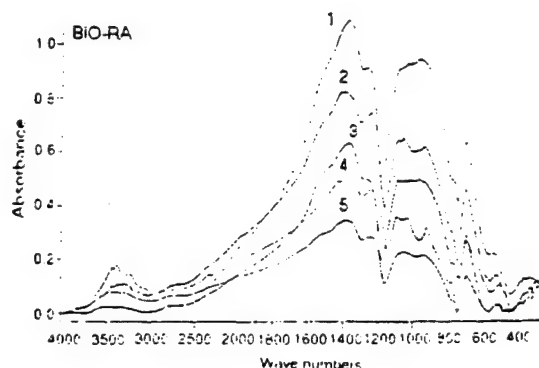
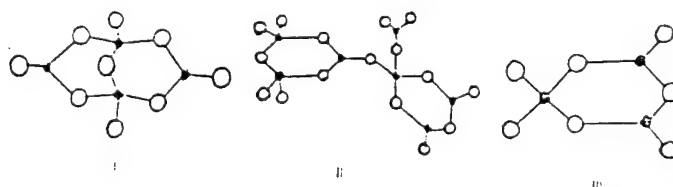


Fig. 3. Infrared spectra of several constituent ratios and melting points

TABLE 3. Relationship Between Constituent Composition Ratio Among Starting Materials, Crystallization Phase, and Molecular Structural Types

Composition of solution (mol)	crystalline phase	anion group	molecular structure
$\text{Li}_2\text{O} : \text{B}_2\text{O}_3$			$\text{BO}_3(\Delta) : \text{BO}_4(\nabla)$ configuration
1 : 2.0	$\text{Li}_2\text{B}_4\text{O}_7$	$(\text{B}_4\text{O}_7)^{2-}$	$(2\Delta + 2\nabla)$
1 : 3.0	$\text{Li}_2\text{B}_4\text{O}_7$	$(\text{B}_4\text{O}_7)^{2-}$	$(2\Delta + 2\nabla)$
1 : 3.5	$\text{Li}_2\text{B}_4\text{O}_7$	$(\text{B}_4\text{O}_7)^{2-}$	$(2\Delta + 2\nabla)$
	$\text{Li}_2\text{B}_2\text{O}_5$	$(\text{B}_2\text{O}_5)^{2-}$	$(4\Delta + 3\nabla)$
1 : 4.0	$\text{LiB}_3\text{O}_6$	$(\text{B}_3\text{O}_6)^{2-}$	$(2\Delta + \nabla)$
1 : 5.0	$\text{LiB}_3\text{O}_6$	$(\text{B}_3\text{O}_6)^{2-}$	$(2\Delta + \nabla)$



melt at different constituent composition ratios. There were  $\text{BO}_4$  and  $\text{BO}_3$  radicals in the LBO melt. The ratio of the quantities of these radicals can be reflected to a certain extent in the peak value intensities of the infrared absorption spectra. We can see that during variation of the constituent composition ratios, a

corresponding variation also occurs in the constituent ratios of  $\text{BO}_3$  and  $\text{BO}_4$  in the melt, thus variation also occurs in the crystallization phase.

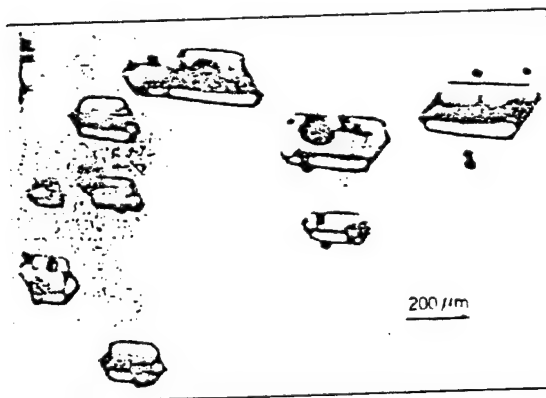


Fig. 4. Negative-crystal inclusions in LBO crystals

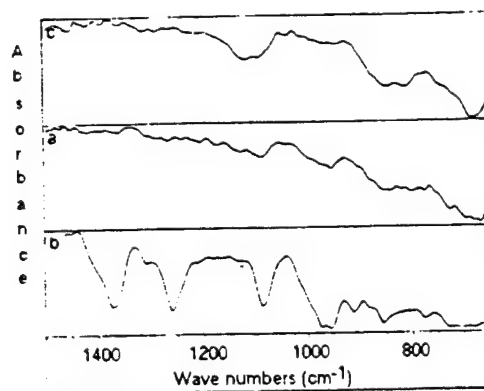


Fig. 5. Curve of infrared absorption spectra in the negative-crystal zone (a), and the perfect zone (b) in LBO crystals, and in LBO glass

### 3.5. Defects of negative crystal inclusions in LBO crystals [48]

Inclusions are a frequent main defect in crystals grown by the

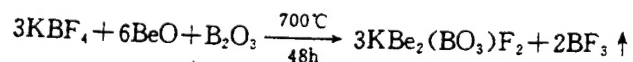
molten salt method. In LBO crystals, we discovered regular shape and directionally arranged inclusions called negative crystals, as shown in Fig. 4. With research observations on negative crystal defects by using x-ray and laser scattering layer analysis methods, such defects were found to be solid. As indicated in the analytical results from using an x-ray microscope, this is a glassy state borate. Fig. 5 shows the results of analyzing the infrared spectra. We can see from the figure that the infrared spectrum (Fig. 5 (a)) at the negative-crystal defect differs from the crystal-state LBO (Fig. 5 (b)), but is the same as the glassy-state LBO (Fig. 5(c)). From the foregoing serial method in the observation analysis, we can deduce that the inclusions of negative crystal inclusions are actually a kind of mother liquid inclusion, which is caused owing to grater temperature fluctuation or concentration of impurities with the constituent supercooling or stepped overhanging. Such mother liquid with greater supercooling state has its temperature slowly lowered during the crystal growth process, to continuously precipitate crystals on the outer wall of the crystal, actually exhibited as a kind of internal growth. Since this internal growth is also inhibited by the surrounding crystal structure, forming negative crystals with a certain crystallization direction and shape. When crystal precipitation ceases, a residue remains and condenses into the glassy-state mother liquid, forming voids due to temperature difference between solid and liquid.

#### IV. Growth of CBO Crystals [49]

Cesium triborate  $\text{Cs}_5\text{B}_3\text{O}_5$  (CBO) is a compound with isoconstituent melting, with the melting point at  $837^\circ\text{C}$ . Therefore, CBO crystals can be grown by the simpler melt pulling method. Wu Yicheng et al. applied the pulling method to grow transparent  $30 \times 20 \times 17 \text{ mm}$  single crystals. The crystal growth was in a resistance oven; the starting materials were analytically pure  $\text{Cs}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$ . According to the mole ratio 1:3 in weight  $\text{Cs}_2\text{CO}_3:\text{B}_2\text{O}_3$ , high-temperature melting was conducted after homogeneous mixing to reduce to the crystallization temperature. Seed crystals were introduced and the temperature was slowly lowered. The crystal rotation rate was approximately 10rpm.

#### V. Growth and Properties of KBBF Crystals

The KBBF melting point was estimated to be above  $1100^\circ\text{C}$ . However, KBBF seriously evaporates and decomposes at temperatures higher than  $800^\circ\text{C}$ , therefore the flux method should be used to grow crystals. The starting materials used to grow KBBF crystals can be prepared as follows: in the first method, pure KBBF is first synthesized by using the following chemical reaction:



then the KBBF obtained is mixed in an appropriate proportion with  $\text{KF}-\text{B}_2\text{O}_3$ . In the second, simpler, method,  $\text{BeO}$  and excess  $\text{KBF}_4$ , as well as a small amount of  $\text{H}_3\text{BO}_3$  are mixed and placed in a platinum crucible, then the mixture is heated in a muffle oven to  $700^\circ\text{C}$  to be maintained for 48h. The crystals are grown with spontaneous

nucleation or by the molten-salt seed crystal method. Transparent crystals with dimensions up to 10x10x1mm were grown from the KBBF-KF-B<sub>2</sub>O<sub>3</sub> and KBF<sub>4</sub>-BeO-B<sub>2</sub>O<sub>3</sub> systems. The appropriate constituent composition ratios are: 1.0 mol KBBF:4.7 mol KF:0.8mol B<sub>2</sub>O<sub>3</sub> and (2.2 to 2.3) mol KBF<sub>4</sub>:1.0 mol BeO: (0 to 0.4) mol B<sub>2</sub>O<sub>3</sub>.

The main difficulty in growing KBBF crystals is due to the fact that the crystal is a compound with an obvious layer structure. Therefore, the crystal exhibits anisotropic growth properties, to grow into a thick crystal that is not easily obtained in the chip-shaped growth method. Therefore, this is an urgent task facing us: how to seek the appropriate flux or blended substance to change the crystal growth properties in order to grow crystals with thickness of practical dimensions.

## VI. Crystal Growth Shape and Negative-Ion Coordination Polyhedron Theoretical Model

Crystal growth shape is a vital factor in studying crystal growth. The crystallization property of a crystal is determined mainly by its internal structure. In modern research on the relationship between crystal shape and internal structure, the most successful theory is the periodic bond chain theory (PBC). This theory was proposed by Harmann and Pardok in 1955 [50]. From the viewpoint of bond energies, they pointed out that crystal formation is affected by strong bonds and chains in the crystal structure. Recently, Zhong Weizhuo et al. proposed a theoretical model stating that the fundamental unit in crystal growth is negative-ion

coordination polyhedron, from the viewpoint of crystallization chemistry. This model was applied to explain satisfactorily the crystallization property of a series of crystals, including BBO and LBO [51-56]. They pointed out that the negative-ion coordination polyhedra on the crystal growth fundamental unit and in the crystal structure are the same. The crystal surface growth rate is related to the rhombic exposure of the angle or surface on crystal surfaces by the negative-ion coordination polyhedra in crystals. Different exposure sites have different receiving capability in growing the fundamental units in solution. When the growing fundamental units connect with the apex angle on the crystal surface, stabilization is optimal, thus the growth rate is rapid. During surface connection, the distance between cations is the shortest, thus having the highest expulsion force, thus resulting in lower stabilization and slower growth rate. During the connection with rhombic exposure, the growth rate is intermediate between the two values mentioned above.

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